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# Origin of Graphite in the Southwestern Grenville Province

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# ORIGIN OF GRAPHITE IN THE SOUTHWESTERN GRENVILLE PROVINCE

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## ABSTRACT

Two graphite deposits in the southwestern Grenville Province are investigated to evaluate the origin of graphitic carbon and test if graphite mineralization is syngenetic or epigenetic. Graphite mineralization in the Bissett Creek deposit is characterized by homogeneously distributed and disseminated graphite flakes (about 1 to 5 mm in size and 2 to 10 vol.%) within graphitic gneisses. Graphite flakes are intergrown with metamorphic minerals, most notably biotite. The Montpellier Graphite showing in Quebec contains graphite concentrations of up to 20 vol.%. In contrast to the disseminated and homogenously distributed graphite in the Bissett Creek Deposit, graphite mineralization at Montpellier forms lenses of variable sizes that occur at the top of a calc-silicate unit and as graphite-rich lenses in biotite-sillimanite rich paragneiss. The $\delta^{13}C$ of graphite ranges from –29 to –17 ‰ at Bissett Creek and from –18 to –14 ‰ at Montpellier. Carbon isotope compositions of graphite from both deposits support a biogenic source for the carbon and the spread in $\delta^{13}C$ can be generated through Rayleigh fractionation. A minor

contribution of inorganic carbon from the devolatilization of carbonate minerals is possible at Montpellier. Mineralization at Bissett Creek and Montpellier is interpreted to represent syngenetic graphite mineralization from organic-rich material during high-temperature metamorphism.

*Keywords*: Graphite, Grenville Province, Carbon isotopes, Metamorphic, Gneiss

## INTRODUCTION

As an industrial mineral, graphite is primarily utilized in the steel industry where it is included in bricks that line furnaces (*e.g.,* refractories) to provide strength and resistance to heat and corrosion, used to line ladles and crucibles, and added to steel to increase strength (Luque *et al.* 2014). Graphite is also used extensively in the automobile industry in gaskets, brake linings and clutch materials. It has a myriad of other industrial uses including electric motors (carbon brushes), batteries, lubricants, pencils, fuel cells, vanadium redox batteries, components of equipment used to generate nuclear and solar energy, golf clubs, hockey sticks, and other sporting goods (*cf.*, Spence 1920, Hewitt 1965, Garland 1987, Mackinnon & LeBaron 1992). Increasing demand for green energy has also made graphite a very attractive exploration prospect because of its abundant use in lithium-ion batteries. Thus, it is important to develop and test genetic models of graphite mineralization, which can be used to prioritize exploration targets.

Graphite deposits are usually divided into three classes. From relatively low to high value, these classes include: amorphous, flake and vein graphite deposits (Spence 1920, Mitchell 1993, Luque *et al.* 2014). Amorphous graphite represents an aggregate of extremely fine lathes. Flake graphite is the scaly or lamellar form of the mineral, commonly found disseminated in

59 metamorphic rocks, such as crystalline limestone, gneisses and schist (*e.g.* Mitchell 1993). Vein
60 graphite is found in veins or fracture systems along intrusive contacts of pegmatites with host
61 limestones and schists (*e.g.* Luque *et al.* 2014).

62 There are currently two main genetic models that describe graphite mineralization. They
63 are the growth of graphite during metamorphic processes, also known as graphitization, and the
64 precipitation of graphite from hydrothermal fluids or melt (Rumble *et al.* 1986a,b, Papineau *et al.*
65 2010a, b, Luque *et al.* 2012, Beyssac & Rumble 2014,). These processes are end members; some
66 graphite deposits are formed through both metamorphism and hydrothermal deposition
67 (Papineau *et al.* 2010a,b, Luque *et al.* 2012). Graphitic carbon deposited from hydrothermal
68 fluids occurs globally, in rocks from all depths in Earth's crust and ranging in age from
69 Precambrian to Tertiary (Rumble 2014). Metamorphic graphite is concentrated in high-
70 temperature metamorphic rocks whereas lower-grade rocks generally contain other carbonaceous
71 material (e.g. coal) in addition to graphite (Okuyama-Kusunose and Itaya, 1987)

72 In the Southwestern Grenville Province, it is unclear if Proterozoic graphite deposits are
73 formed through metamorphic or hydrothermal processes or some combination of both. This is
74 important information for understanding the genesis of graphite (*e.g.*, Luque *et al.* 2014) and
75 linking metamorphism into global geochemical cycles of carbon (*e.g.*, Galy *et al.* 2008). Also,
76 understanding the mineralization mechanisms and the influence of different rock types and
77 structures can be used to develop new exploration targets for graphite deposits (*e.g.*, Soman *et al.*
78 1986). In this contribution, the origin of two graphite deposits in the southwestern Grenville
79 Province (the Bissett Creek deposit in Ontario and the Montpellier graphite showing in Quebec)
80 are evaluated using a combination of field observations, petrology, lithogeochemistry and carbon
81 isotope analysis of graphite. These locations were chosen because the rocks at the Bissett Creek

deposit contain no carbonate minerals whereas graphite mineralization at the Montpellier showing is spatially associated with carbonates. Two possible sources for carbon that form graphite in metamorphic terranes are the breakdown of organic material to graphite at temperatures at and above the amphibolite facies (e.g. Landis, 1971), and the decarbonation of carbonate minerals and precipitation of graphite at amphibolite- to graulite-facies conditions (e.g. Santosh and Omori, 2008). Therefore, this investigation of the Bissett creek deposit and the Montpellier showing allows the two main models of graphite mineralization to be evaluated for two different styles of graphite deposits in the southwestern Grenville Province.

## REGIONAL GEOLOGY

Most graphite mineralization in Canada is located in the Grenville Province of Southern Quebec and Central Ontario (Spence 1920, Hewitt 1965, Garland 1987, Simandl 1989, Mackinnon & LeBaron 1992). The metallogeny of the structural zones of the Grenville province was well defined by Sangster *et al.* (1992). The southwestern Grenville Province consists of granitic gneisses, metavolcanic rocks, metasedimentary schists and impure marbles that were deformed and metamorphosed during the Grenville orogen (Wynne-Edwards 1972, Carr *et al.* 2000, Rivers *et al.* 2012).

The two graphite deposits studied here are located in separate parts of the southwestern Grenville Province. The Bissett Creek deposit is part of the Mesoproterozoic gneisses of the Central Gneiss Belt (Carr *et al.* 2000), which is also known as the Ottawa River Gneiss Complex (Rivers & Schwerdtner 2015). In the vicinity of the deposit, the geology is interpreted to represent reworked rocks of the former Laurentian margin (*e.g.*, Carr *et al.* 2000). The Montpellier graphite showing is found in the Composite Arc Belt, which represents

allochthonous Mesoproterozoic volcanic arcs and sedimentary rocks that accreted to the southeast margin of Laurentia during the Grenville orogen (*e.g.*, Carr *et al.* 2000).

## GEOLOGY OF THE BISSETT CREEK GRAPHITE DEPOSIT

### *Location*

The Bissett Creek graphite property (Fig. 1) belongs to the Northern Graphite Corporation of Ottawa and it is easily accessible by the Trans-Canada Highway (Highway 17), approximately 53 km east of the town of Mattawa. All mining claims are located in Maria Township, Ontario in the County of Renfrew, Province of Ontario.

### *Field relationships and lithogeochemistry*

Graphite mineralization at the Bissett Creek deposit is characterized by homogeneously distributed graphite flakes (about 1 to 5 mm in size) within biotite-rich quartzofeldspathic gneisses (Fig. 2a; Taner 2010, 2013). The graphitic gneisses are subdivided into: (1) biotite-rich quartzofeldspathic gneiss, (2) diopside–tremolite–biotite graphitic gneiss, and (3) graphite-poor sillimanite–garnet gneiss, which occurs at the boundary between the graphitic and barren gneisses. Where observed, the contacts between each of the different graphitic gneiss units are gradational over centimetres to metres. The total thickness of graphitic gneisses, from west to east, varies from 25 m to 90 m, as determined by drilling. At the surface, the graphitic gneisses form a distinctive recessive weathering unit (generally red-orange to pale yellow-brown weathering) and are commonly exposed along rock cuts, hilltops and occasional cliff faces (Fig. 2b). When weathered, graphite flakes are easily picked out of the rock.

A barren quartzofeldspathic gneiss with no graphite occurs structurally above and below the graphitic gneiss. Drilling intersections internal to the deposit vary in thickness from 1 to 20 m. In drill core, sharp contacts between the barren gneiss and the graphitic gneiss suggest an intrusive relationship. The gneissic units are intruded by metre-scale pegmatites (Fig. 2c), and in one location, by a metre-scale lamprophyre dyke (Fig. 2d).

The pegmatite unit is a light grey to pinkish, quartz-feldspar rich rock with some large dark brown flakes of biotite and rare pyrite. Pegmatite zones locally contain rare graphite mineralization in the form of flakes intercalated with biotite. Biotite enrichment occurs within the contact zones with the host gneisses.

The lamprophyre dyke unit is fine grained, dark green and exhibits sharp intrusive contacts with the graphitic and barren gneiss units. The lamprophyre dykes do not contain graphite mineralization. Lamprophyre dykes are subvertical and generally strike east–west (Fig. 2d).

Foliations are shallowly dipping to sub-horizontal across the property. The graphitic gneiss has a moderate dip to the east from 5 to 20 degrees and the high-grade layer dips 20 to 30 degrees south. Gignac et al. (2012) report two generations of folding present on the property. The primary deformation event produced isoclinal folds (Fig. 2a), which were then refolded during a second event into large open folds (Gignac *et al.* 2012).

*Petrographic observations*

The biotite-rich, quartzofeldspathic graphitic gneiss is fine to medium-grained, light to dark grey, and contains between 2 and 10 vol.% homogeneously disseminated, graphite flakes (Fig. 3a). The biotite-rich, quartzofeldspathic gneiss is composed of centimetre-to decimetre-

scale, quartz-feldspar rich leucosomes that have lower amounts of graphite and display augen-gneiss textures. Leucosomes alternate with millimetre- to centimetre-scale biotite and graphite-rich layers. Biotite-rich layers contain between 4 and 10 vol.% graphite that is homogeneously distributed (Fig. 4a). Graphite flakes are 1–5 mm in length (Fig. 4b) and are intimately associated with biotite (Fig. 4c). Disseminated sulfides (1–2 vol.%, mostly pyrrhotite) occur within biotite-rich layers. Garnet and muscovite are present in some samples from this unit.

The diopside–tremolite–biotite gneiss is fine- to medium-grained and is composed of quartz–feldspar-rich layers (mm to dm) that alternate with diopside–tremolite–biotite–graphite rich layers (Fig. 3b). It is located in the upper part of the mineralized graphite zones at Bissett Creek. Graphite comprises 3 to 6 vol.% of this unit and is homogeneously distributed as disseminated graphite flakes (Fig. 4d). Trace amounts (1–2 vol.%) of disseminated sulfide minerals (mostly pyrrhotite) are also present. Some parts of this unit also contain garnet, but it is frequently found in close association with pegmatite intrusions. Minerals are generally granoblastic in this unit.

The biotite–sillimanite–garnet gneiss unit is medium-grained and contains a well-defined foliation defined by the parallel alignment of biotite and sillimanite lathes (Fig. 3c). It is composed of millimetre- to centimetre-scale, leucocratic layers that alternate with millimetre- to decimetre-scale, biotite–sillimanite–garnet-rich layers. The melanocratic layers are composed of quartz and feldspar with up to 15 vol.% biotite, up to 15 vol.% sillimanite and up to 5 vol.% garnet. Graphite flakes are rare and are usually associated with disseminated pyrite and pyrrhotite (1–2 vol.%).

The barren gneiss unit is found structurally above and below the graphitic gneiss units. This unit is composed of pink quartzofeldspathic leucosome that alternates with relatively biotite-rich melanosome (Fig. 3d). This unit contains no graphite.

*Economic Geology*

The graphitic carbon contents of select graphitic units reported in Gignac *et al.* (2012) are summarized in Table 1 and displayed in Figure 5. Samples were analyzed for graphitic carbon at SGS Laboratories using the CSA05V analytical package, which uses a roast/coulometry method. The diopside–tremolite–biotite gneiss shows a range of graphitic carbon contents from ~1 to 3 wt.%. The biotite-rich quartzofeldspathic gneiss unit contains between ~1 and 4 wt.% graphitic carbon. The median graphitic carbon content of the biotite-rich quartzofeldspathic gneiss is ~1% higher than the diopside–tremolite–biotite gneiss (Fig. 5). Graphite particles generally contain 20–30 vol.% interlayered mica (Fig. 4c). Measured resources of graphite at the Bissett Creek deposit are estimated at 69.8 million tonnes grading 1.74% graphitic carbon based on a 1.02% graphitic carbon cutoff grade (Gignac *et al.* 2012, Leduc 2013). The inferred resource is 24 million tonnes grading 1.65% graphitic carbon with a 1.02% graphitic carbon cutoff (Gignac *et al.* 2012, Leduc 2013). Liberated graphite flakes occur as oval to sub-rounded particles ranging from 1 to 6 mm in diameter.

## GEOLOGY OF THE MONTPELLIER GRAPHITE OCCURRENCE

*Location*

192 The Montpellier Graphite showing is located northeast of Lavergne Lake close to the
193 village of Montpellier in Ripon Township, within the Composite Arc Belt of the Grenville
194 Province (Fig. 1).
195
196 *Field Relationships*
197 The geology of the Montpellier graphite showing is summarized in a simplified
198 stratigraphic column in Figure 6. The geology consists of metasedimentary rocks (quartzite,
199 paragneiss, and calc-silicate), metavolcanic rocks (both mafic and felsic), and granitic gneisses
200 and an ortho-amphibolite. These units have experienced polyphase folding (Fig. 7a, b). All units
201 are crosscut by a diabase dyke.
202 The graphite-rich unit contains up to 20 vol.% graphite and forms lenses of variable sizes
203 at the top of a calc-silicate unit and also within biotite–sillimanite–garnet-rich paragneiss (Fig.
204 6). Disseminated graphite also occurs in the calc-silicate unit (Fig. 7a). The contact between the
205 graphite-bearing paragneiss unit and the overlying impure quartzite unit is irregular (Fig. 7c).
206 The graphite showing is exposed at surface along a vertical cliff about 4 m high and over
207 a distance of 100 m. This zone is strongly oxidized (Fig. 7b), contains sulfide minerals (mostly
208 pyrrhotite and lesser amounts of pyrite), and it is very friable and weathered along this exposure.
209 Graphite is visible as dark flakes within the competent gneissic unit and when it is weathered,
210 similar to Bissett Creek, graphite flakes are easily picked out of the rock. Graphite flakes are
211 preferentially aligned with the gneissosity. In this particular part of the showing the gneissosity
212 dips shallowly to the west (Taner 1989).
213
214 *Petrographic observations*

The graphite-rich unit contains up to 15–25 vol.% graphite. Two types of mineralization are distinguished: (1) a massive zone with uniformly distributed graphite flakes; and (2) a zone where the graphite flakes are concentrated in nodules. The massive zone occurs in both calc-silicate and paragneiss units whereas the nodular zone is only found in the paragneiss unit.

The calc-silicate unit contains 3–5 vol.% disseminated graphite (Fig. 7a). This unit is composed of variable quantities of recrystallized carbonate (calcite and/or dolomite, about 30–50 vol.%; Fig. 8a), diopside (20–30 vol.%), plagioclase (20–30 vol.%) and minor amounts of wollastonite, scapolite, phlogopite, sulfides (pyrrhotite and/or pyrite), and disseminated graphite flakes (3–5 vol.%). Locally, the amount of disseminated graphite can reach 20 vol.% (Fig. 8b). Disseminated grains (or blebs) of sphalerite (mm to cm in size) occur within the calc-silicate unit. Graphite mineralization is stratiform at the top of calc-silicate unit.

Biotite–sillimanite–garnet-rich paragneiss lies beneath the most graphite-rich horizon (Fig. 6). From the contact with the lower calc-silicate unit, the proportion of graphite flakes progressively increases up section within biotite-rich paragneiss. This unit contains coarse-grained garnet and biotite. Graphite is intergrown with biotite (Fig. 8c, d) and is found along cracks in garnet (Fig. 8c).

*Economic Geology*

The graphitic carbon contents of the graphitic units from the main outcrop are summarized in Table 2. Samples were analyzed for graphitic carbon at SGS Laboratories using the CSA05V analytical package. Graphitic carbon contents range from ~1 to 20 wt.%, with more than half the values above 10 wt.%. Individual graphite grains are millimeters in length (Fig. 8e, f). The average grade of this main outcrop is 13.6 wt.% graphitic carbon. Graphite mineralization

238 continues beneath the impure quartzite unit and within the biotite–sillimanite–garnet-rich
239 paragneiss. Mineralized zones vary in thickness from 0.2 to 4.8 m and are laterally continuous
240 over 100 m. Graphite-rich zones are composed of friable material that form lenses with graphite
241 flakes of about 1 mm in size.
242
243 CARBON ISOTOPE ANALYSIS OF GRAPHITE
244 *Methods*
245 Twelve samples were selected for carbon isotope analysis of graphite (eight from Bissett
246 Creek and four from Montpellier). Six samples from Bissett Creek were sampled from drill core,
247 one from a hand sample (BC-0) and one was a graphite concentrate from the mill (BC-M). Four
248 samples were collected from drill core from the Montpellier prospect. With the exception of the
249 mill sample from Bissett Creek, all rocks were crushed by hand and graphite was hand-picked
250 under a binocular microscope. For the mill sample, an aliquot of the graphite product was used.
251 The carbon isotopic compositions of the graphite separates were analyzed at the
252 Laboratory for Stable Isotope Science at the University of Western Ontario. The refractory
253 nature of the graphite presented challenges for some samples and hence a range of analytical
254 approaches were used. First, all samples were analyzed using a Costech 4010 Elemental
255 Analyzer connected in continuous flow mode to a Thermo Scientific Delta$^{PLUS}$ XL mass
256 spectrometer. About 0.2 – 0.6 mg of sample was wrapped in tin capsules, prior to combustion at
257 1020°C. These analyses were conducted twice, once without and once with addition of ~1 mg of
258 $V_2O_5$. The latter was added as extra oxidant to facilitate combustion. Samples were calibrated to
259 VPDB using the accepted values for USGS40 and USGS41 (Qi *et al.* 2003).

Ten of twelve samples were also analyzed using the conventional method of Boutton (1991). Graphite (~1.2 – 1.5 mg) was added to a quartz tube, along with 600 mg of CuO and 500 mg Cu. The evacuated and sealed quartz tubes were then combusted at 900°C for two hours and cooled overnight. Because visible graphite still remained in the quartz tubes, they were combusted again for a further 3 hours at 1000°C, prior to being allowed to cool overnight. The carbon dioxide was then released, cryogenically purified, and then analyzed using a Micromass Optima dual inlet isotope ratio mass spectrometer. Samples were calibrated to VPDB using accepted values for NBS-19 and L-SVEC (Coplen *et al.* 2006a).

All results are reported in the normal delta notation relative to VPDB (Coplen et al., 2006b). Comparable results were obtained for all methods. A $\delta^{13}C$ of –15.9 ± 0.2‰ (2SD; n=8) was obtained for USGS24 graphite, as compared to its accepted value –16.0 ± 0.1‰ (2SD). A $\delta^{13}C$ of –25.7 ± 0.2‰ (SD; n=5) was obtained for the internal laboratory carbon standard, as compared to its accepted value of –25.7 ± 0.2‰ (SD). Reproducibility (SD) of samples ranged from ±0.1 to ±0.7 ‰, and averaged ±0.3‰ (Table 3).

*Results*

The $\delta^{13}C$ of graphite in this study is summarized in Table 3 and in Figure 9. For the Bissett Creek deposit, the carbon isotope compositions have a wide range, varying from –29 to –17‰ and yield an average value of –23‰. For the Montpellier showing, measured compositions range from –18 to –14‰ with an average of –16‰.

## DISCUSSION

*Metamorphic versus hydrothermal graphite*

283 Graphite deposits may form through metamorphism of carbonaceous matter or by
284 precipitation from carbonic fluids and/or melts (Pasteris 1999, Luque *et al.* 2014). Syngenetic (or
285 'metamorphic') graphite deposits are generally found in high-grade metamorphic rocks and the
286 graphite is disseminated in flake form (Luque *et al.* 2014). Individual graphite grains usually
287 contain impurities of metamorphic minerals (Mitchell 1993) and graphite is found within the
288 matrix assemblage and not in pore spaces (Bernard & Papineau 2014). The carbon content of
289 graphite in these deposits generally ranges from 75 to 97% and individual crystals are generally
290 millimeters in size (Mitchell 1993).
291 Epigenetic (or 'vein graphite') deposits are also usually found in high-grade metamorphic
292 rocks, but they are spatially associated with fracture or vein sets (*e.g.* Rumble and Hoering
293 1986b, Kehelpannala & Francis 2001). Graphite in these deposits is nearly pure with average
294 carbon contents of ~99% (Mitchell 1993). Graphite occurs as nearly monomineralic veins or
295 nodules that are centimeters to decimeters in size (Barrenechea *et al.* 2009, Luque *et al.* 2014).
296 Individual crystals are large and generally centimeters in size (Mitchell 1993).
297 Four specific petrographic and field observations support the metamorphic (syngenetic)
298 model for graphite mineralization at both Bissett Creek and Montpellier. First, graphite is
299 disseminated throughout the graphitic units and is not located along fracture sets or associated
300 with veins. At Montpellier, some graphite occurs in nodules, but graphite represents less than 30
301 vol.% of the mineral assemblage, which is inconsistent with nearly monomineralic veins that are
302 characteristic of epigenetic graphite deposits. Second, individual graphite flakes from Bissett
303 Creek and Montpellier can contain up 20–30 vol.% interlayered biotite. Again, this is
304 incompatible with the relatively pure (~99%) graphite from epigenetic deposits. Third, individual
305 graphite flake sizes are on the order of millimeters, which is consistent with other syngenetic

306 graphite deposits (*e.g.* Mitchell 1993). Fourth, graphite flakes are intergrown with metamorphic
307 minerals including biotite and garnet (Fig. 4c, 8c), which supports a metamorphic origin for the
308 graphite. Taken together, these different petrological and field observations are most consistent
309 with a metamorphic model of graphite mineralization and are incompatible with the epigenetic
310 model of graphite deposition.
311
312 *Origin of carbon responsible for graphite mineralization*
313 There are three main sources of carbon that form graphite: (1) carbon from organic
314 materials, (2) carbon from the devolatilization of carbonate minerals, and (3) carbon from mantle
315 sources (Luque *et al.* 2012). Each of these sources has a characteristic range of $\delta^{13}C$. Most
316 Proterozoic organic matter has $\delta^{13}C$ that ranges from –40 to –10 ‰ (Schidlowski 1988, 2001).
317 The $\delta^{13}C$ of carbon derived from the mantle is approximately –5 ‰ (*e.g.*, Deines 2002). Marine
318 carbonates generally have compositions around ~0 ‰ (*e.g.,* Keith & Weber 1964). The
319 compositions of these sources are summarized in Figure 9. The carbon isotope compositions of
320 these sources, however, can only be compared with measured graphite $\delta^{13}C$ if the latter has not
321 been significantly fractionated during metamorphism.
322 There are two main processes that can modify the carbon isotope composition of graphite
323 from that of its source during metamorphism. Devolitilization of organic material can shift $\delta^{13}C$
324 by up to 5‰ (*e.g.,* Barker & Friedman 1969, Wada *et al.* 1994), usually due to the release of
325 isotopically light carbon during the production of methane (*e.g.,* Luque *et al.* 2012). Most
326 studies, however, document shifts of ~ 1‰ (*e.g.,* Hahn-Weinheimer & Hirner, 1981). The second
327 process is carbon isotope exchange between graphite and inorganic material (e.g. carbonate
328 minerals).

329 The presence of two carbonic species during metamorphism (organic carbon and
330 carbonate minerals and/or carbonic fluid derived from their breakdown) with different carbon
331 isotope compositions leads to isotopic exchange during metamorphism. The amount of isotope
332 fractionation during carbon isotope exchange is mainly a function of temperature (Dunn &
333 Valley 1992). This process is particularly important at relatively low metamorphic temperatures.
334 For example, the calibration of Dunn & Valley (1992) for calcite–graphite isotope exchange
335 predicts shifts of ~10‰ at 400°C and ~6‰ at 600°C. High-temperature metamorphism (e.g.
336 amphibolite and granulite facies) promotes efficient isotope exchange between these minerals
337 and isotope fractionation is expected to be only a few per mil (*e.g.,* Dunn & Valley 1992). This is
338 supported by graphite in metamorphic rocks that has $\delta^{13}C$ similar to the primary organic material
339 inferred to be the source of carbon (*e.g.,* Barker & Friedman 1969, Weis *et al.* 1981, Crawford &
340 Valley 1990). Because mineralization at Bissett Creek and Montpellier occurs in amphibolite-to
341 granulite-facies gneisses (see Rivers *et al.* 2012 and references therein), the carbon isotope
342 compositions of graphite from Bissett Creek and Montpellier are expected to be within a few per
343 mil of that of the source of the carbon.
344 The $\delta^{13}C$ compositions of graphite from both deposits show a continuum of values from
345 –29 to –14‰ that is consistent with carbon derived from organic materials (Schidlowski 1988,
346 2001). Graphite from Montpellier is enriched in $^{13}C$ relative to graphite from Bissett Creek,
347 which may reflect a more $^{13}C$-rich source of carbon or isotopic exchange between carbonate
348 minerals and graphite. Although carbonate minerals are not currently present at the Bissett Creek
349 deposit, the diopside–tremolite–biotite assemblage in the calc-silicate unit was likely derived
350 from decarbonation reactions involving the breakdown of calcite and dolomite (*e.g.*, Valley &
351 Essene 1980). Graphite from a calc-silicate sample (MP-3) has the highest $\delta^{13}C$ of the Bissett

352 Creek samples (Table 3) and plots within the range of measured compositions from the
353 Montpellier occurrence (Fig. 9). Therefore, the continuum of graphite $\delta^{13}C$ compositions may
354 represent a measure of the contribution of isotope exchange between organic carbon and
355 carbonic fluids released during the breakdown of carbonate minerals during prograde
356 metamorphism.

357 An alternative model to explain the continuum of $\delta^{13}C$ for graphite at Bissett Creek is
358 Rayleigh fractionation of metamorphic fluids derived from an initially homogeneous $\delta^{13}C$
359 reservoir (e.g. Ray and Ramesh, 2000; Ray, 2009). Figure 10 presents the results of a multi-
360 component Rayleigh fractionation model (Ray, 2009); this model considers graphite that
361 precipitated from a mixed $CO_2$–$CH_4$ metamorphic fluid at 700°C derived from a reservoir with
362 $\delta^{13}C$ of –26 ± 2‰. The initial molar ratio of $CH_4$ and $CO_2$ ($r_{CH4–CO2}$) in the source fluid was set at
363 0.99 to extend the evolution to a nearly complete exhaustion of the source (e.g. Ray, 2009).

364 Modeled graphite $\delta^{13}C$ ranges from –32‰ initially up to –17‰ when 1% of the fluid
365 remains (Fig. 10). Therefore, Rayleigh fractionation of an initially homogenous carbon reservoir
366 can also explain the spread of $\delta^{13}C$ at Bissett Creek. Considering the paucity of carbonate
367 minerals and the relatively minor amount of calc-silicates at Bissett Creek, the Rayleigh
368 fractionation model is our preferred interpretation for the continuum of $\delta^{13}C$ of graphite from this
369 locality.

370 The abundance of carbonate units at the Montpellier occurrence may have resulted in
371 higher graphite $\delta^{13}C$ than graphite from the carbonate-deficient Bissett Creek Deposit. Similar to
372 Bissett Creek, however, the spread in $\delta^{13}C$ of graphite may also represent Rayleigh fractionation
373 of an initially homogeneous source. In either interpretation, the carbon responsible for graphite
374 mineralization is mostly biotic in origin at both Montpellier and Bissett Creek.

Most studied graphite deposits in the southwestern Grenville Province are spatially associated with carbonate units (*e.g.,* Mackinnon and LeBaron 1990, 1992). The results of this study suggest that the source of carbon for graphite precipitation is principally biogenic even in the carbonate-rich Montpellier occurrence. Therefore, the contribution of carbon from the decarbonitization of carbonate minerals may be relatively minor. It remains to be tested if this holds true for other carbonate-hosted graphite deposits in the Grenville Province.

## CONCLUSIONS

The Bissett Creek deposit and the Montpellier showing in the southwestern Grenville Province contain disseminated graphite mineralization and graphite morphologies that are consistent with a metamorphic origin. Carbon isotope compositions of graphite from both deposits support a biogenic source for the carbon and the spread in graphite $\delta^{13}C$ can be generated through a Rayleigh fractionation process. A minor contribution of carbon from the devolatilization of carbonate minerals is also possible at Montpellier. In general, the results of this study suggest that graphite deposits in the southwestern Grenville Province reflect graphite precipitation from metamorphic fluids derived from the breakdown of biogenic material.

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## FIGURE CAPTIONS

FIG. 1. Simplified map of the Grenville Province with the location of the Bissett Creek graphite deposit and the Montpellier graphite showing (modified from Rivers *et al.*, 2012). ABT: Allochthon Boundary Thrust, CABTZ: Composite Arc Boundary Thrust Zone, CAB: Composite Arc Belt, CGB: Central Gneiss Belt, FAB: Frontenac–Adirondack Belt, PSD: Parry Sound Domain.

FIG. 2. Field relationships of the Bissett Creek deposit. (a) Folded leucosome in the barren (no graphite) gneiss unit. (b) Gossan at the surface of a graphitic gneiss. (c) Pegmatite cutting foliation in the host graphitic gneiss. (d) Sub-vertical lamprophyre dyke cutting foliation in the host graphitic gneiss.

FIG. 3. Gneisses at the Bissett Creek deposit. (a) Biotite-rich quartzofeldspathic gneiss with graphite-rich melanosome. (b) Diopside-tremolite-biotite gneiss with graphite-rich melanosome. (c) Biotite-sillimanite-garnet gneiss with graphite- and biotite-rich melanosome. (d) Barren gneiss with pink leucosome.

FIG. 4. Microstructures of graphitic gneisses from the Bissett Creek deposit. (a) Quartzofeldspathic gneiss with disseminated graphite flakes (plane-polarized light). (b) Coarse-grained graphite in biotite-rich quartzofeldspathic gneiss (plane-polarized light). (c) Intergrown biotite and graphite in the biotite-rich quartzofeldspathic gneiss (plane-polarized light). (d) Disseminated graphite in a diopside–tremolite gneiss in plane polarized light (ppl; top left) and cross-polarized light (xpl; bottom right).

FIG. 5. Graphitic carbon contents of the two dominant graphitic units at the Bissett Creek deposit. Whiskers extend to the lowest and highest datum inside 1.5 times the interquartile range

FIG. 6. A simplified stratigraphic column of the geology of the Montpellier Graphite showing (modified from Taner 1989). 1. Impure quartzite, containing locally biotite-rich paragneiss (1a) and some monzonitic gneiss (1b). 2 Biotite–sillimanite–garnet-rich paragneiss with some graphite-rich zones. 3 Graphite rich zones (10 to 20 wt.% graphitic carbon). 4. Calc-silicate unit; (4a) containing 3-5 wt.% graphitic carbon; (4b) diopside-rich marble; (4c) marble. 5. Biotite-rich paragneiss without graphite flakes. 6 Hornblende and biotite-rich gneiss. 7. Granitic gneiss. 8. (Ortho-) amphibolite. 9. Late diabase dyke.

FIG. 7. Rock types and field relationships of the Montpellier Graphite showing. (a) An exposure of the main graphite-rich calc-silicate unit (UTM 4902260m E, 5077102m N; NAD83, Zone 17). Graphite is disseminated throughout the outcrop. (b) Recumbently folded calc-silicate unit (c) Irregular contact between the quartzite and paragneiss units.

FIG. 8. Microstructures of graphitic gneisses from the Montpellier graphite showing. (a) Combination of plane-polarized (ppl; top left) and cross-polarized (xpl; bottom right) images showing the association of carbonate minerals with graphite flakes in the calc-silicate unit. (b) Thin section scan showing disseminated graphite flakes in the calc-silicate unit (plane-polarized light). (c) Garnet associated with biotite and graphite in the paragneiss unit (plane-polarized

light). (d) Thin section scan showing coarse-grained graphite flakes intergrown with biotite (plane-polarized light). (e) Coarse-grained graphite in the graphite-rich zone (plane-polarized light). (f) Thin section scan (plane-polarized light) showing oriented graphite flakes in a graphite-rich layer.

FIG. 9. Summary of $\delta^{13}C$ of graphite from Bissett Creek and Montpellier along with the variation in $\delta^{13}C$ of different sources of carbon. The compositions of organic carbon (at ~1 Ga) and recent marine carbonate are from Schidlowki (2001). The compositions of mantle graphite are compiled from Deines et al. (1991), Pearson et al. (1994), Viljoen (1995) and Schulze (1997). On the box-and-whisker plots, the whiskers extend to the lowest and highest datum inside 1.5 times the interquartile range and outliers are outside of this range.

FIG. 10. Results of a multicomponent Rayleigh fractionation model (Ray, 2009) for a starting source composition of $\delta^{13}C = -26 \pm 2‰$, a temperature of 700°C and $r_{CH4\text{-}CO2} = 0.99$. The graphite-fluid and $CO_2$-$CH_4$ fractionation factors at this temperature are from Scheele and Hoefs (1992) and Horita (2001).

**TABLE 1.** Graphitic carbon contents of select samples from Bissett Creek.

| Sample ID: | Rock Type | Graphitic C (wt. %) |
|---|---|---|
| BC03 | Bt-Rich QF gneiss | 1.29 |
| BC11 | Bt-Rich QF gneiss | 3.63 |
| BC12 | Bt-Rich QF gneiss | 3.15 |
| BC13 | Bt-Rich QF gneiss | 3.16 |
| BC14 | Bt-Rich QF gneiss | 2.92 |
| BC15 | Bt-Rich QF gneiss | 3.88 |
| BC16 | Bt-Rich QF gneiss | 2.76 |
| BC17 | Bt-Rich QF gneiss | 0.86 |
| BC18 | Di–Trem gneiss | 1.05 |
| BC19 | Pegmatite | 1.38 |
| BC20 | Di–Trem gneiss | 2.02 |
| BC21 | Di–Trem gneiss | 1.33 |
| BC22 | Bt-Rich QF gneiss | 1.36 |
| BC23 | Di–Trem gneiss | 1.06 |
| BC24 | Di–Trem gneiss | 1.98 |
| BC25 | Bt-Rich QF gneiss | 2.01 |
| BC26 | Di–Trem gneiss | 0.92 |
| BC27 | Bt-Rich QF gneiss | 2.10 |
| BC28 | Di–Trem gneiss | 2.01 |
| BC29 | Di–Trem gneiss | 3.07 |

623 **TABLE 2.** Graphitic carbon content of samples from Montpellier.
624

| Sample | Graphitic C (wt. %) |
|---|---|
| MPG-01 | 0.82 |
| MPG-02 | 1.94 |
| MPG-03 | 14.4 |
| MPG-04 | 2.69 |
| 805 | 9.75 |
| 806 | 9.86 |
| 807 | 10.66 |
| 808 | 14.8 |
| 809 | 16.36 |
| 810 | 20.42 |
| 811 | 19.51 |

625
626
627 **TABLE 3.** Carbon isotope results for graphite from Bissett Creek and Montpellier.
628

| Sample | Rock Type | $\delta^{13}C$ (‰, VPDB) |
|---|---|---|
| *Bissett Creek* | | |
| BC-0 | Bt-Rich QF gneiss | –24.8 ± 0.2 (n=8)* |
| BC-M | Bulk sample from mill | –21.2 ± 0.2 (n=2) |
| BC-10 | Bt-Rich QF gneiss | –29.1 ± 0.1 (n=3) |
| BC-11 | Bt-Rich QF gneiss | –18.8 ± 0.7 (n=3) |
| BC-12 | Bt-Rich QF gneiss | –26.7 (n = 1) |
| BC-13B | Bt-Rich QF gneiss | –17.4 ± 0.2 (n=3) |
| BC-14 | Bt-Rich QF gneiss | –22.5 ± 0.6 (n=4) |
| BC-15 | Bt-Rich QF gneiss | –20.2 (n = 1) |
| *Montpellier* | | |
| MP-2 | Paragneiss | –14.3 ± 0.5 (n=4) |
| MP-3 | Calc-silicate gneiss | –13.6 (n = 1) |
| MP-4 | Paragneiss | –16.9 ± 0.2 (n=5) |
| MP-5 | Paragneiss | –17.7 ± 0.2 (n=5) |

629 *error reported as SD; n = number of analyses on graphite from each sample.

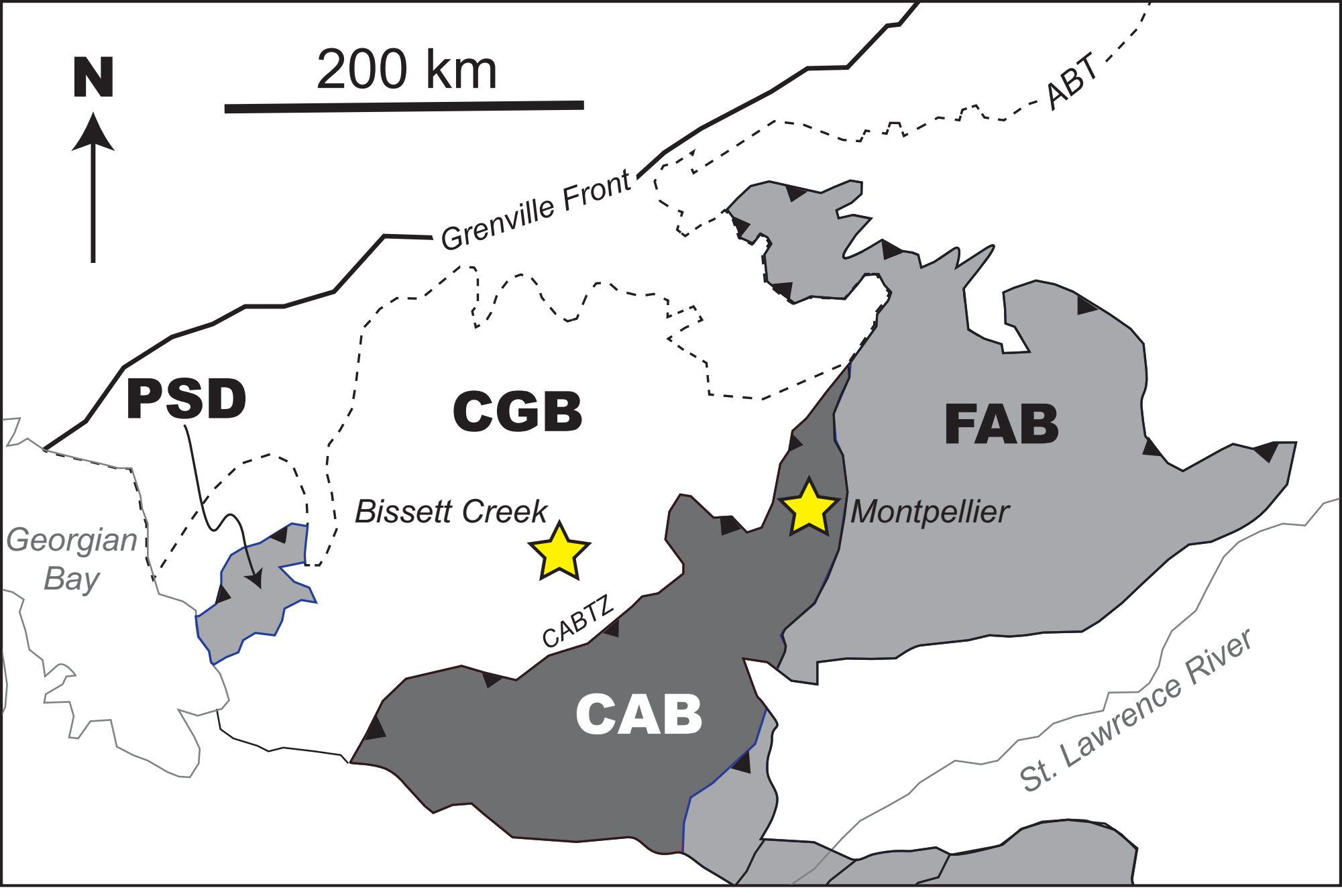
N
200 km
ABT
Grenville Front
PSD
CGB
FAB
Bissett Creek
Montpellier
Georgian Bay
CABTZ
CAB
St. Lawrence River

Figure 1

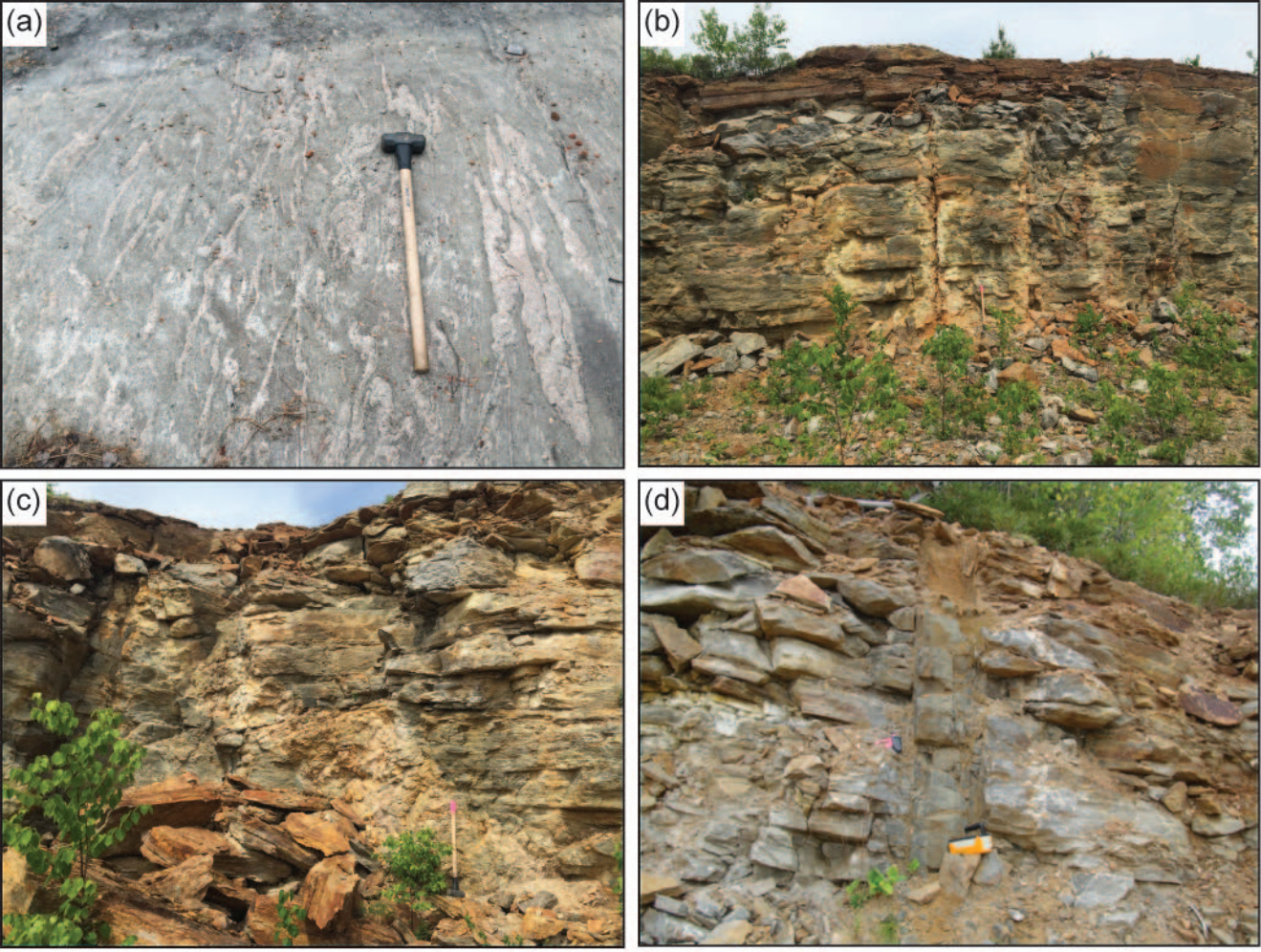


Figure 2

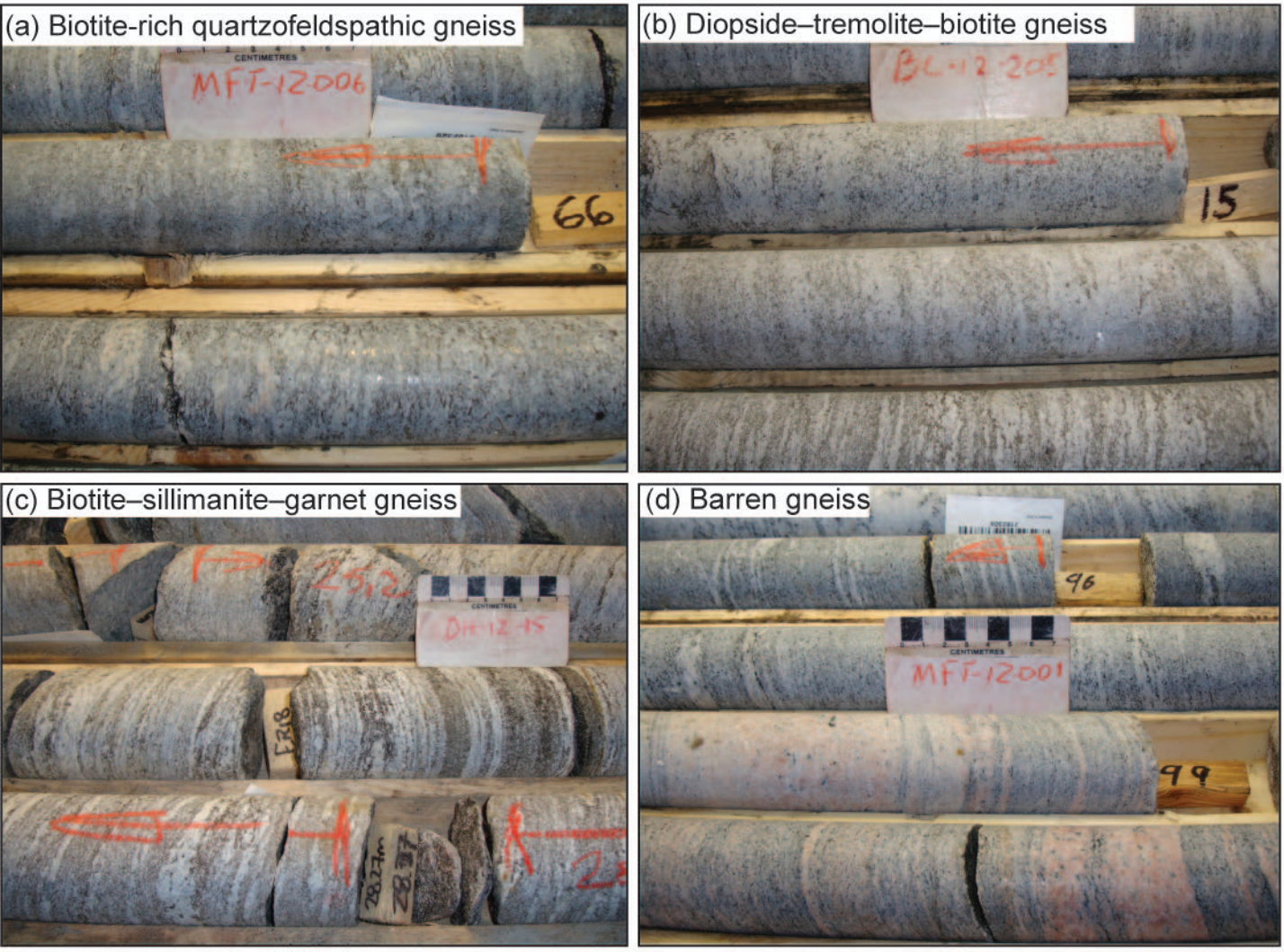
(a) Biotite-rich quartzofeldspathic gneiss
MFT-12006
66
(b) Diopside–tremolite–biotite gneiss
15
(c) Biotite–sillimanite–garnet gneiss
DH-12-15
(d) Barren gneiss
96
MFT-12001
99

Figure 3

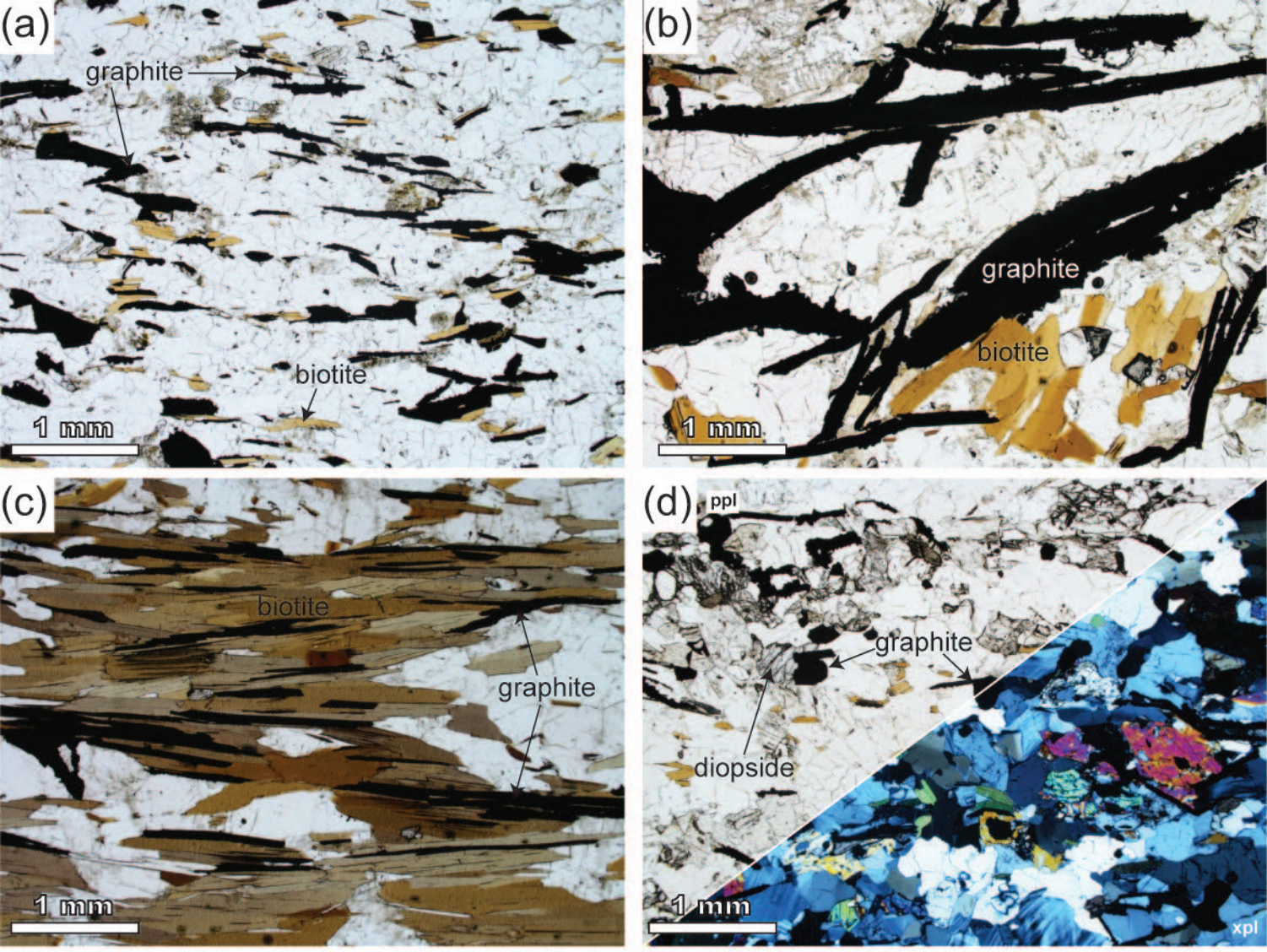
(a)
graphite
biotite
1 mm
(b)
graphite
biotite
1 mm
(c)
biotite
graphite
1 mm
(d)
ppl
graphite
diopside
1 mm
xpl

Figure 4

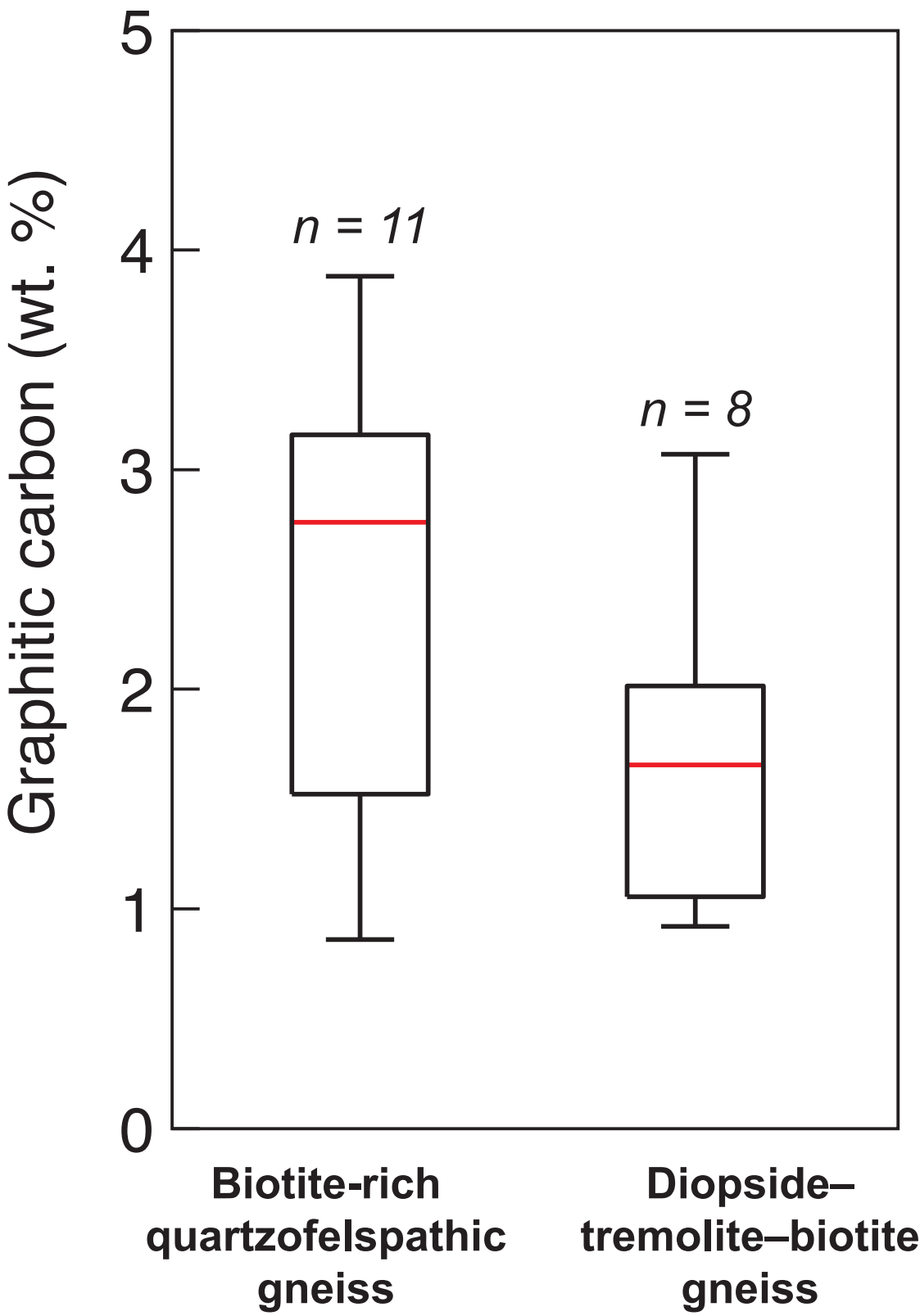
5
4
3
2
1
0
Graphitic carbon (wt. %)
n = 11
n = 8
Biotite-rich quartzofelspathic gneiss
Diopside–tremolite–biotite gneiss

Figure 5

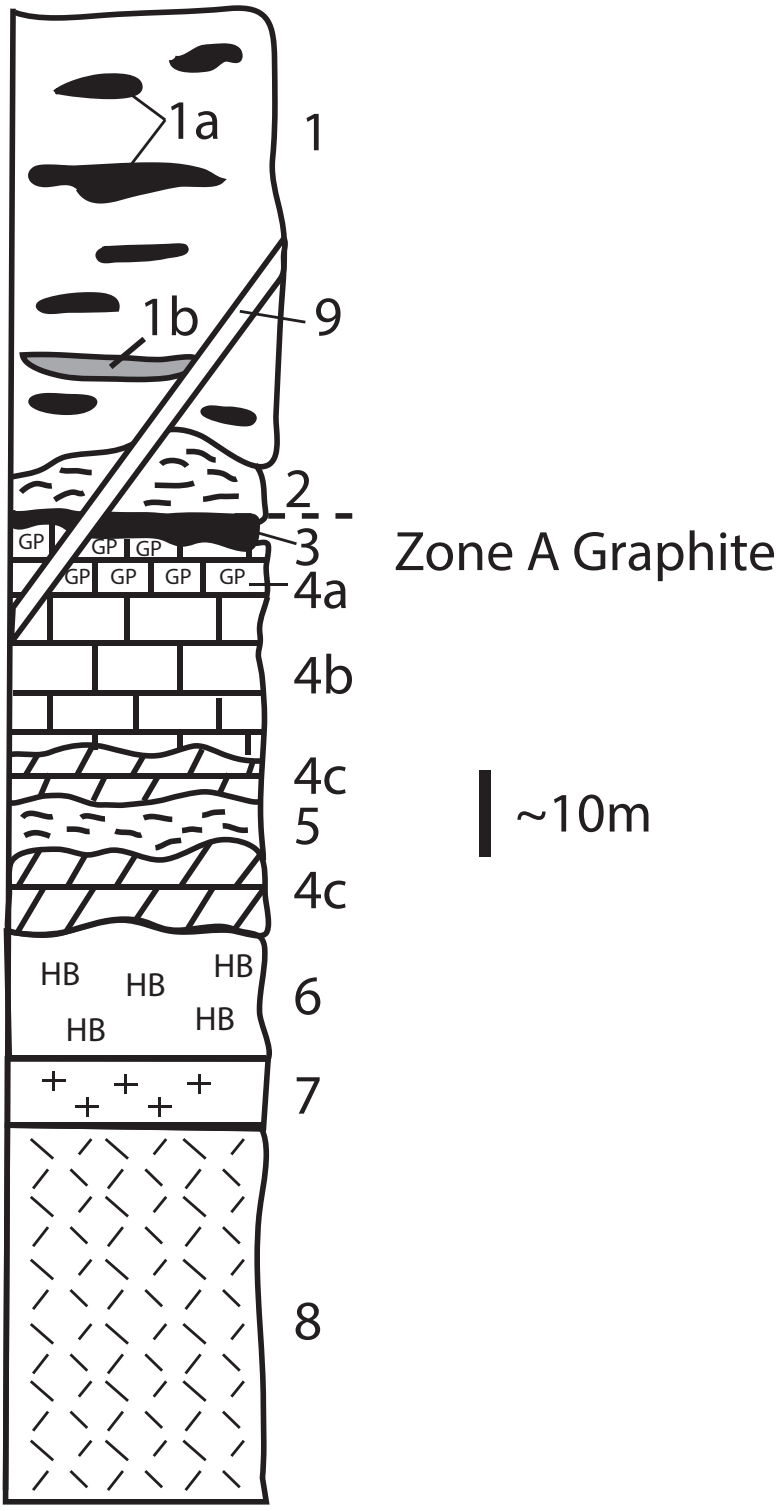
1a
1
1b
9
2
3
Zone A Graphite
GP
GP
GP
GP
GP
GP
GP
4a
4b
4c
5
~10m
4c
HB
HB
HB
HB
HB
6
7
8

Figure 6

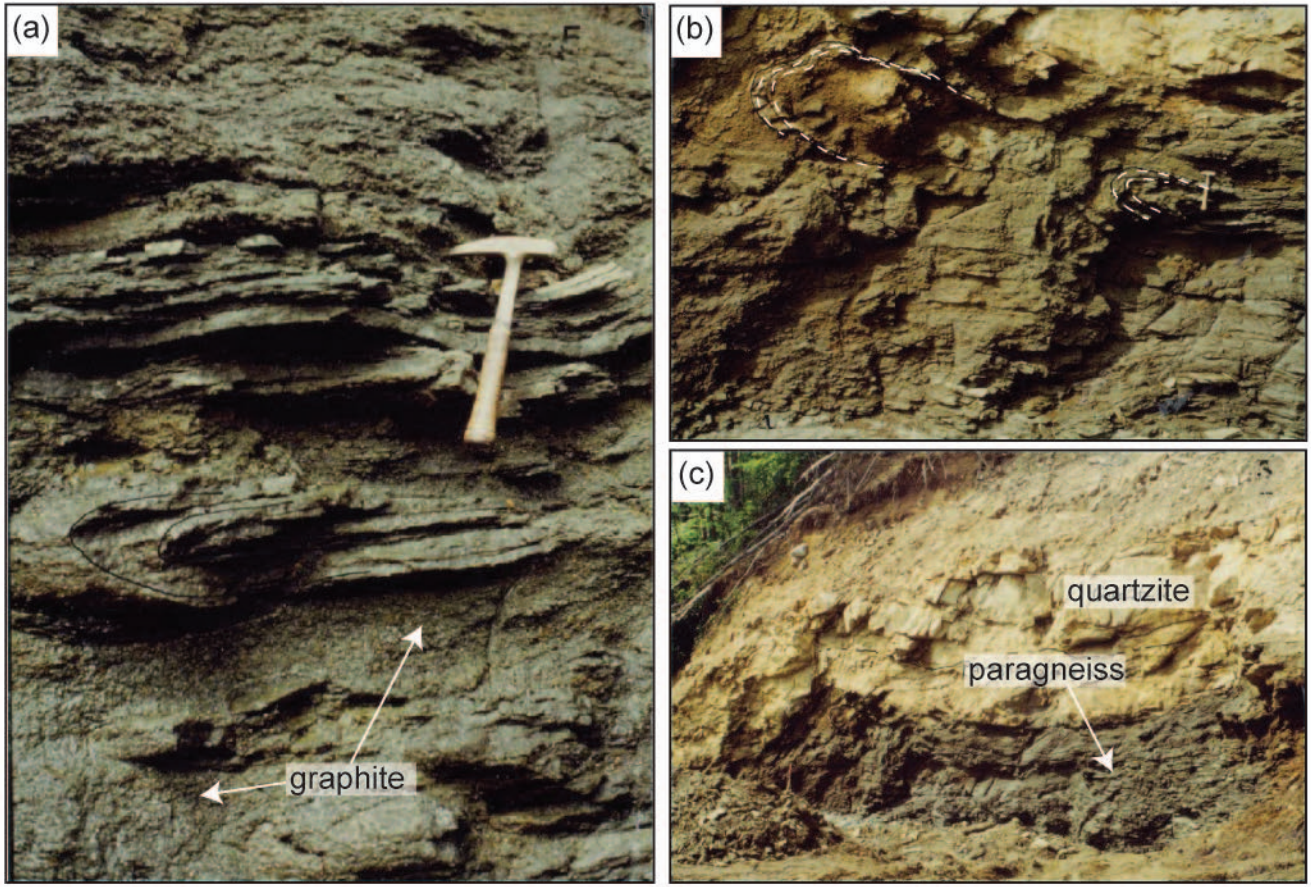


Figure 7

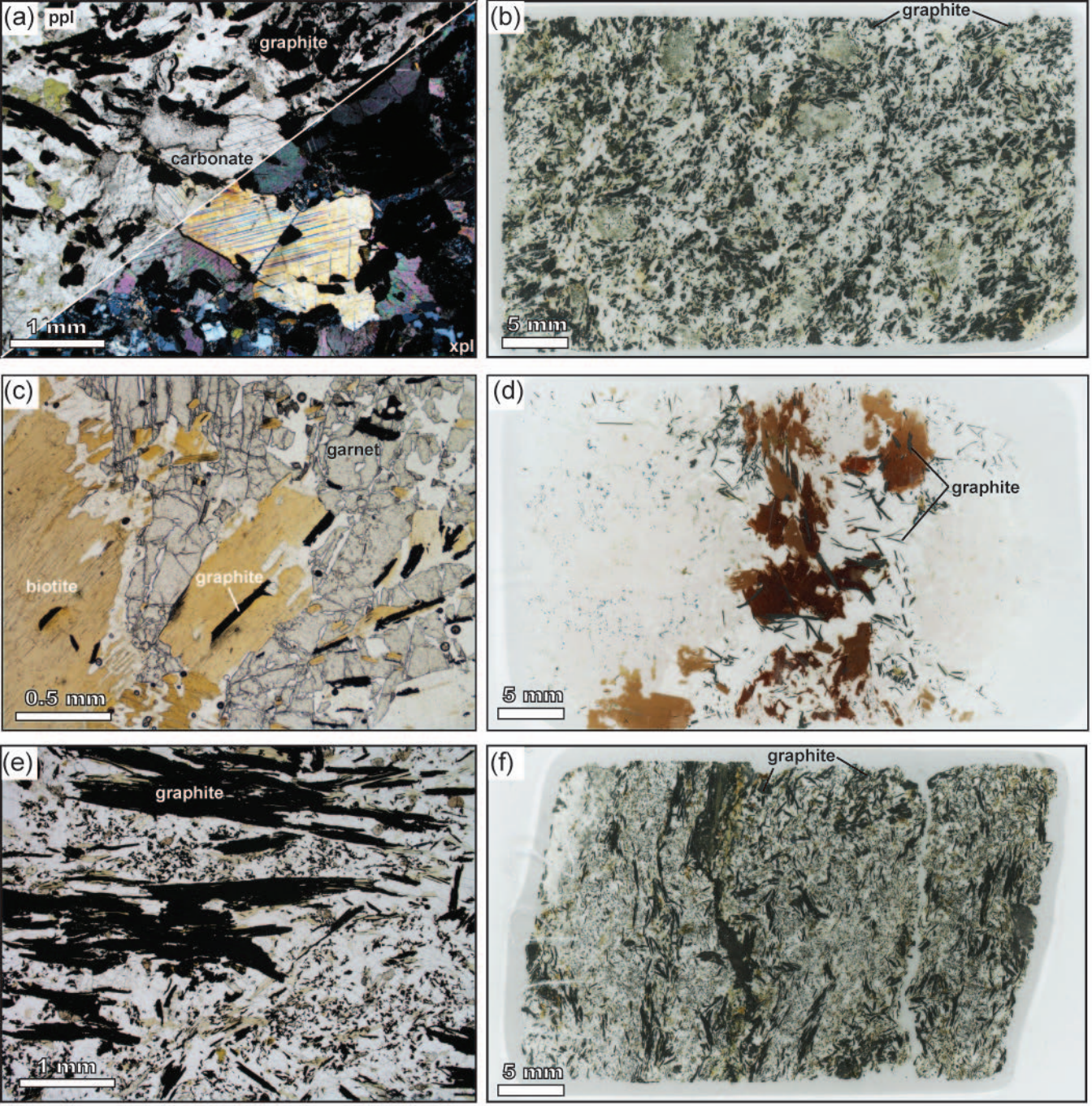
(a)
ppl
graphite
carbonate
1 mm
xpl
(b)
graphite
5 mm
(c)
garnet
biotite
graphite
0.5 mm
(d)
graphite
5 mm
(e)
graphite
1 mm
(f)
graphite
5 mm

Figure 8

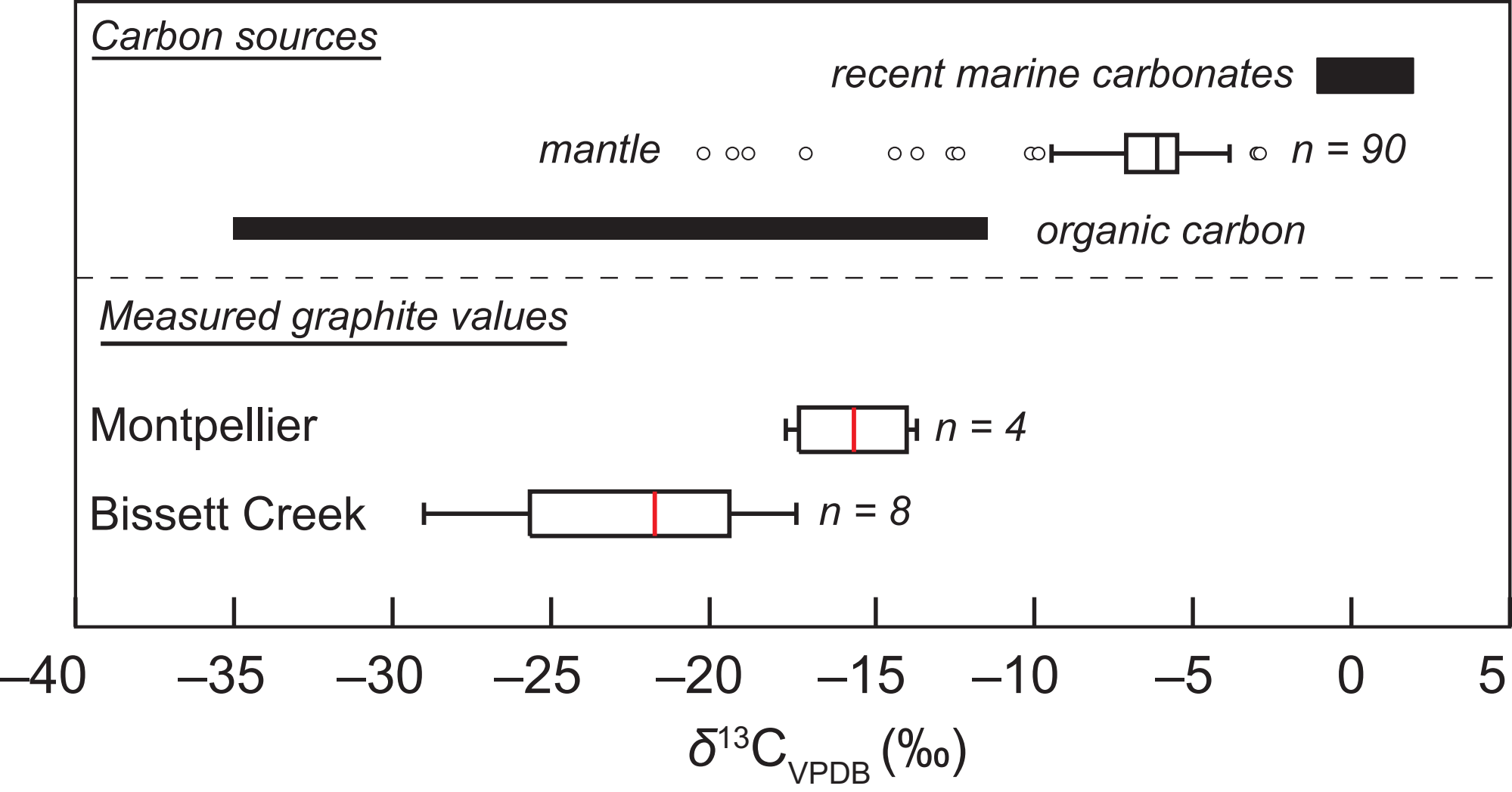
Carbon sources
recent marine carbonates
mantle
n = 90
organic carbon
Measured graphite values
Montpellier
n = 4
Bissett Creek
n = 8
–40
–35
–30
–25
–20
–15
–10
–5
0
5
δ13CVPDB (‰)

Figure 9

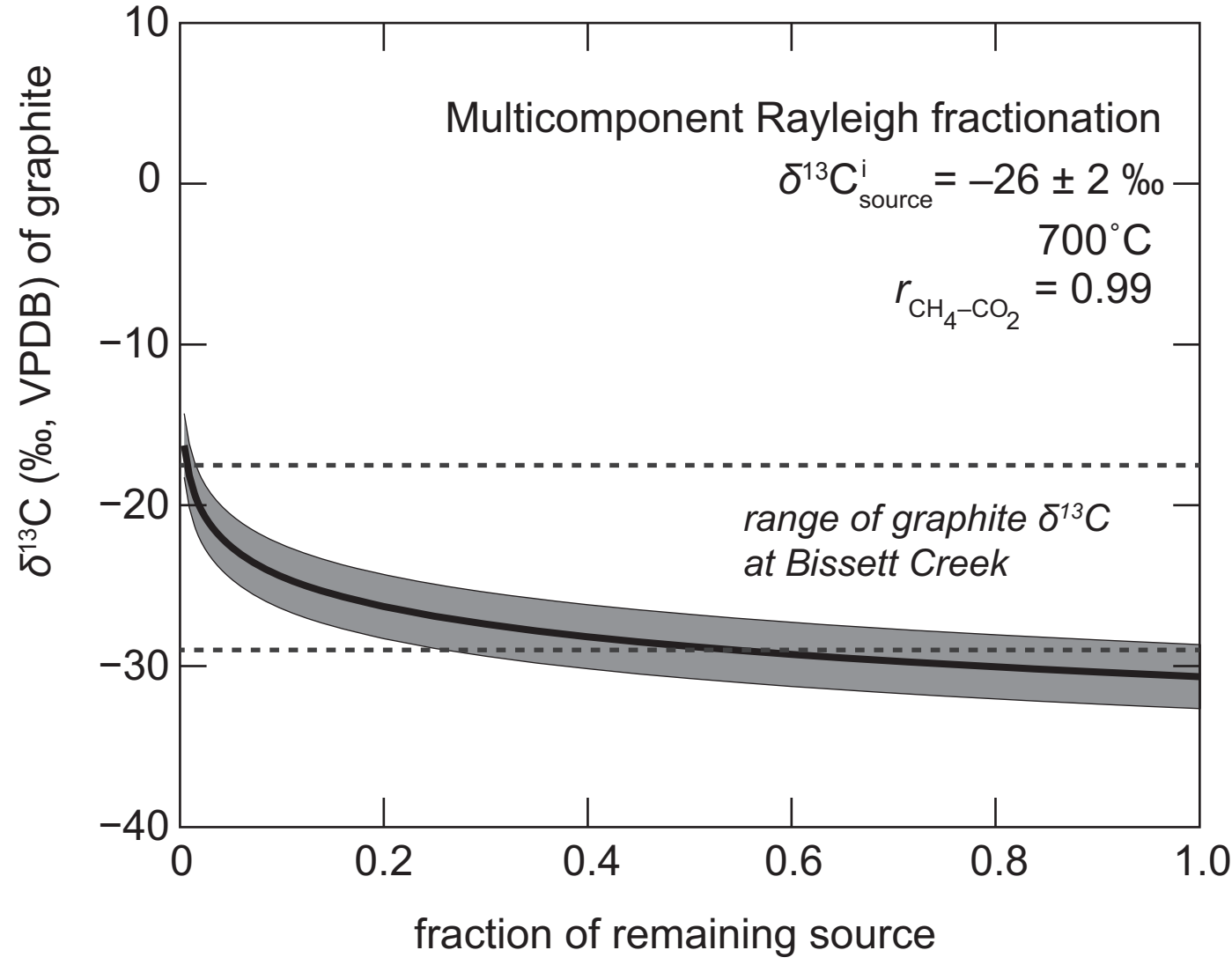
Multicomponent Rayleigh fractionation
$\delta^{13}C^{i}_{source}$ = –26 ± 2 ‰
700˚C
$r_{CH_4–CO_2}$ = 0.99
range of graphite $\delta^{13}C$ at Bissett Creek
$\delta^{13}C$ (‰, VPDB) of graphite
fraction of remaining source
10
0
−10
−20
−30
−40
0
0.2
0.4
0.6
0.8
1.0

**Figure 10**